

# Elementary mechanisms governing the dynamics of silica

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A full understanding of glasses requires an accurate atomistic picture of the complex activated processes that constitute the low-temperature dynamics of these materials. To this end, we generate over five thousand activated events in silica glass, using the activation-relaxation technique; these atomistic mechanisms are analysed and classified according to their activation energies, their topological properties and their spatial extend. We find that these are collective processes, involving ten to hundreds of atoms with a continuous range of activation energies; that diffusion and relaxation occurs through the creation, annihilation and motion of single dangling bonds; and that silicon and oxygen have essentially the same diffusivity.

Glassiness is a dramatic slowing down of the kinetics of a liquid as the temperature decreases below some typical value. Experiments have yielded considerable information about the macroscopic character of this phenomenon, but very few techniques provide the local probe needed to understand its microscopic origin [1–3]. On the theoretical side, significant progress has been made recently in understanding the supercooled region, but little is known about the atomistic nature of the relaxation and diffusion dynamics taking place at temperatures below the glass transition [4]. Using a new Monte Carlo technique, the activation-relaxation technique, we map in detail the activated processes of  $g$ -SiO<sub>2</sub> taking place at low temperatures.

The activation-relaxation technique (ART) is a method that allows an efficient sampling of activated processes (events) in complex continuous systems [5,6]. Moves are defined directly in the configurational energy landscape and can reach any level of complexity required by the dynamics; they can involve hundreds of atoms crossing barriers as high as 25 eV. In a two-step process, a configuration is first brought from a local minimum to an adjacent saddle point and then relaxed to a new minimum. Such an event is shown in figure 1. Each event is accepted or rejected following a standard Metropolis procedure. In this work, we study two independent runs on 1200-atom cells of SiO<sub>2</sub>, modeled with the screened-Coulomb potential of Nakano *et al.* [7,8] which has been shown to give realistic structures and a good account of a number of dynamical properties. We prepare these runs starting from randomly packed unit cells, and relax them through 5000 ART iterations. This procedure ensures absence of correlation, both with the crystalline state as well as between runs. After relaxation, a further 5000 ART iterations are performed on each cell. Slightly more than half of these iterations show a clean convergence to a saddle point, providing a database of 5645

events. An analysis of these events can give us a unique glimpse at the basic nature of activated mechanisms in this material.

We checked for systematic effects caused by the initialization procedure or by the potential used: a comparison with events from a shorter run, starting from an MD-prepared 576-atom sample, indicates that the nature of the events is independent of the preparation mode; a comparison with events from a shorter run in which the van Beest potential was used, with parameters as in [10], indicates that, unless stated otherwise, the results presented here are at least qualitatively similar between these potentials.

The efficiency of ART does not depend directly on the height of the activation barrier or the complexity of the move. The likelihood for a particular event to be sampled by ART, however, is not clearly related to the preferences of nature; entropic considerations, for instance, are left out. This draw-back is not present in molecular dynamics (MD). However, the time scales accessible to MD are limited by the phonon time scale: events in  $g$ -SiO<sub>2</sub> can only be generated with some efficiency if the simulations are performed at elevated temperatures of 4000 K or more [11]; events sampled at these high temperatures are likely to provide an incomplete representation of those occurring below the glass transition. Our approach is therefore to generate a whole distribution of events with ART, and to obtain an overview of the possible types of activated mechanisms in  $g$ -SiO<sub>2</sub>, by classifying these in terms of energy, defects or topological changes. Further study of the details of the energy landscape will be necessary in order to simulate the dynamics of low temperature configurations.

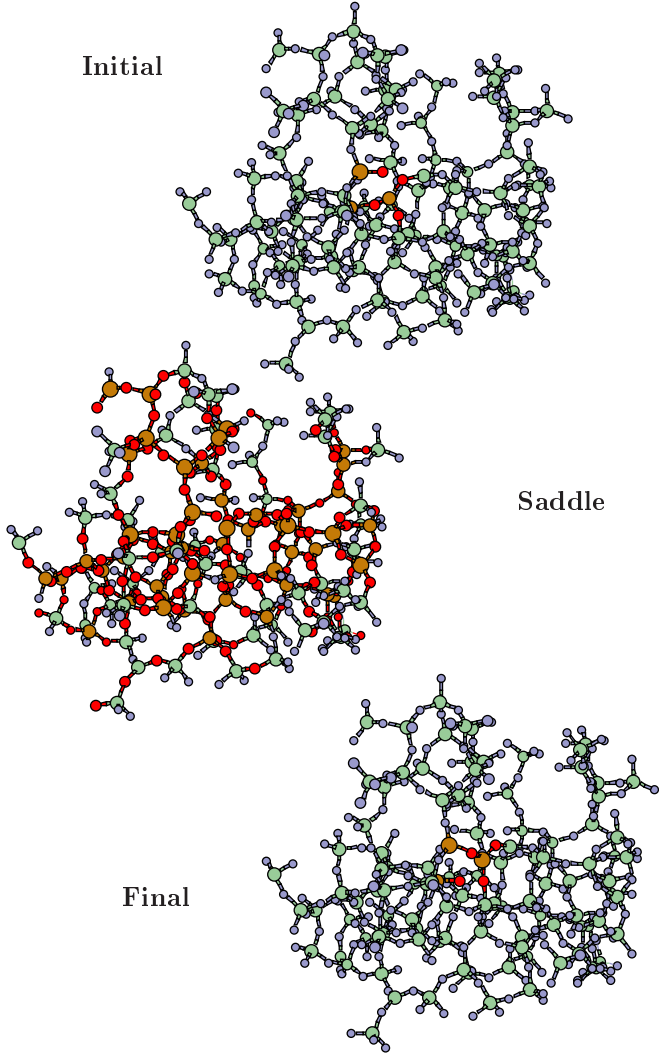


FIG. 1. An event takes place in two stages: the activation from the initial minimum (top) to a saddle point (middle), and the relaxation from there to the final minimum (bottom). For clarity, we have depicted only the 187 atoms that move more than  $0.1 \text{ \AA}$ , plus their nearest neighbors. Large circles are Si atoms, small ones O. In the top and bottom figures, the few atoms that are actually involved in the change of topology, plus their neighbors, are identified by a different color; this particular event is the hopping of a dangling bond on an O to a near neighbor. In the middle figure, the different coloring separates the atoms involved from their immobile neighbors.

During the events acquisition, the configurational energy decreases by about 30 meV per atom. The density of coordination defects fluctuates but does not show a clear trend. With the Nakano potential, the samples have roughly the right density for  $q\text{-SiO}_2$  and about one percent of the bonds between O and Si are missing, compared to perfect coordination. The defects produced are almost uniquely dangling bonds; we do not find any homopolar bond nor, consequently, any superoxide radical or Frenkel pair [1,12]. The van Beest potential [9], that

we used for comparison, tends to produce dense phases and its cut-off needs to be finely tuned to get the right density. Even in that case, it favors overcoordination [10].

We first look at properties averaged over the whole database. Figure 2 shows broad and continuous distributions of the activation barriers and the energy asymmetries (initial to final minimum energy difference). We find that the height of the barrier and the asymmetry of the well are only weakly correlated.

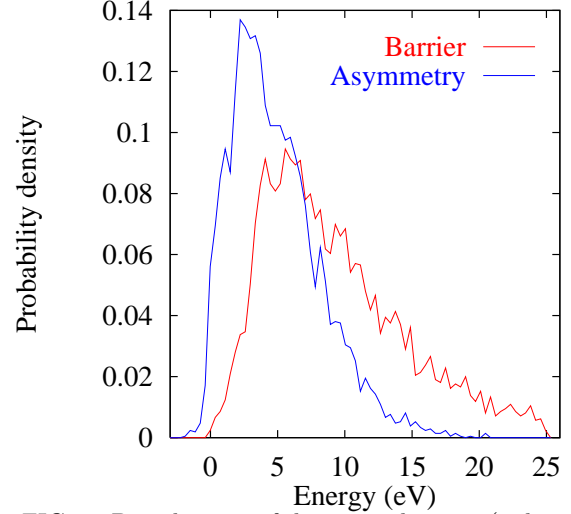


FIG. 2. Distributions of the energy barriers (red curve) and asymmetries (blue curve), obtained from the database of all events. Both distributions are continuous; no gap is seen. The barrier distribution peaks around 5 eV and extends well beyond the physically relevant values, but also displays a significant weight below 5 eV. The asymmetry distribution is narrower, and peaks around 2.5 eV. A small fraction of the events show a negative asymmetry, *i.e.* lower the energy. One expects this fraction to be small, since the configurations are well relaxed. Because of the exponential nature of the activation process, the presence of high energy barriers and states is irrelevant because they are not sampled on normal time scales; it is the low energy part of the spectrum which determines the dynamics.

Besides the barrier, the spatial extend of events is another important quantity. For each event, we determine the number of atoms displaced by more than a threshold distance  $r_c$ . The number of atoms participating in an event depends of course on the value of this threshold. Typically, an event is accompanied by a local volume contraction or expansion. In elastic media, the displacement of the surrounding atoms decreases quadratically away from the center of the event. The number of atoms moving more than a cut-off distance  $r_c$  will therefore decrease as  $r_c^{-3/2}$ , as long as  $r_c$  is in the elastic regime, and the number of atoms much smaller than the sample size; in our case, this scaling is obeyed between 0.05 and 1  $\text{\AA}$ . In figure 3 we plot this distribution for a threshold of  $r_c = 0.1 \text{ \AA}$ , the typical vibrational amplitude of silicon at room temperature. As can be seen from this figure,

events typically involve the motion of hundreds of atoms with simultaneous diffusion of both species to varying degrees: diffusion therefore should not be thought of in terms of elemental jumps but of complex rearrangements.

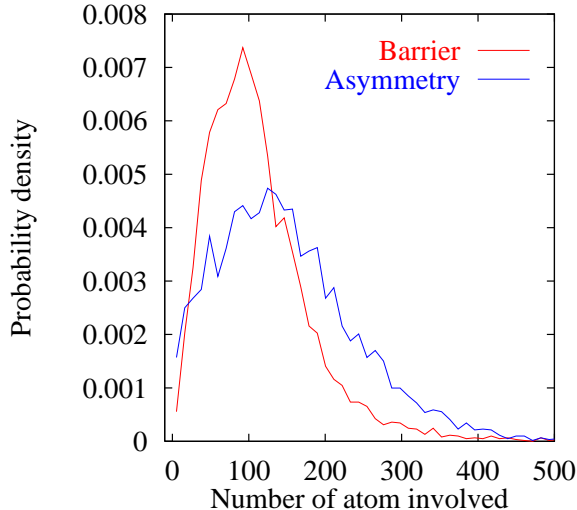


FIG. 3. Distribution of the number of atoms involved in events, *i.e.*, the number of atoms that have moved more than 0.1 Å, from the initial minimum to the saddle point (red curve) and to the final minimum (blue curve). The number of displaced atoms increases as one moves from the saddle point to the new minimum. An event involves typically between 50 and 250 atoms, but a significant number of events involve up to 300 atoms and more. This shows that relaxation in glasses is a collective phenomenon, in agreement with experimental results by Jérôme and Commandeur [13], but different from the related material *a*-Si where only about 40 atoms are typically involved in events [18]. The size of these events puts a lower bound on the number of atoms necessary in numerical simulations to avoid large finite-size effects.

In terms of correlation, larger events are not found to require a higher activation energy: size and energetics are almost entirely uncorrelated. Moreover, no correlation is found between the distance by which Si or O move and the corresponding activation barriers; Si and O have thus the same activation energy.

These results provide a consistent picture for macroscopic diffusion. Theoretical work by Limoge [14] suggests that the effective activation energy should be around the maximum of its distribution, *i.e.*, here, about 5 eV [15]. A similar activation energy was found by Litton and Garofalini for O and Si in MD simulations of molten silica, although the diffusion mechanism described is different from what we see, probably due to the high temperature of the simulations (from 4800 to 7200 K) [11]. Experiments report activation energies of 6.0 eV for Si [16], obtained in electrically fused quartz, and 4.7 eV for O, with a much smaller prefactor [17], obtained in vapor-phase deposited amorphous silica. The difference in experimental activation energies might be caused by the different sample preparation techniques,

resulting in different types of impurities [11].

More microscopic information on the nature of the events can be obtained by studying the topology of the network. For this purpose, we divide the events into three distinct categories: *perfect events* where only perfectly coordinated atoms change neighbors, *conserved events* that involve only diffusion of coordination defects (dangling and floating bonds) and events that create or anneal coordination defects.

Amorphous Si and *g*-SiO<sub>2</sub> are thought to be conceptually similar, both described by Zachariasen's continuous random networks. However, while perfect events play a central role for both relaxation and self-diffusion in *a*-Si [18], they are rare in *g*-SiO<sub>2</sub>: the strong ionicity of SiO<sub>2</sub> enforces chemical ordering, so that atomic exchanges have to occur at the second neighbor level, inducing more strain or larger topological rearrangements than in *a*-Si. Perfect events comprise only about one percent of the total number produced. A third of these events involves local topological rearrangements, mostly two Si exchanging a pair of neighboring O. Such moves can only happen with a relatively low energy barrier if the local rigidity of the network is reduced by nearby undercoordinated atoms. Two thirds of the perfect events do not involve a topological modification but simply some slight local rearrangement, with displacements on the order of 0.1 Å and asymmetries of about 10<sup>-4</sup> eV. Such events could be candidates for tunneling states.

We find 906 conserved events, *i.e.*, events describing the diffusion of defects. Such defects are almost exclusively dangling bonds, on both Si (*E'* centers) and O (non-bridging oxygens), although a few highly energetic floating bonds on O are also present. We see no sign of point defects, which would show themselves by a strong spatial correlation between dangling or floating bonds. Events describe overwhelmingly single-dangling-bond diffusion mechanisms. The simplest of these is a jump of a dangling bond from one atom to its neighbor, an example of which is given in Figure 1. More complex events are also seen, involving jumps to the second or third neighbor, or local rearrangements along a loop. All these mechanisms have relatively well defined barriers and asymmetries. From their statistics we can obtain structural information. For instance, a comparison of near-neighbor dangling bond diffusion involving different topological rearrangements shows that the average cost of creating a 3-fold ring in silica is 1.5 ± 0.2 eV. This value is larger than the 0.25 – 0.81 eV of *ab-initio* calculations on fully relaxed molecules [19,20], suggesting that the local strain on the network caused by topological disorder can affect significantly their effective energy.

More than 80 percent of the events produced involve the creation or the annihilation of coordination defects, with a wide spectrum of energies and configurations. Events with a low barrier and asymmetry, the ones determining the dynamics, are often topologically simple, like

the annihilation of one or two pairs of dangling bonds or their creation. In effect, the creation (or annihilation) of a pair of defect costs (saves) much less energy than would be naively thought by simply considering the breaking of a bond in a crystal or a molecule: the elastic energy stored in the network will often counter the bonding energy. Contrary to what is found in crystalline silica, the creation of a defect in the glass can have an activation energy and asymmetry that is comparable to those associated with their diffusion. For example, creating a pair of dangling bonds in order to remove a 3-fold ring costs only about 0.4 eV, much less than what would be expected in an unstrained environment.

The above results provide the following picture regarding relaxation and diffusion in  $g$ -SiO<sub>2</sub>. Mechanisms responsible for relaxation and diffusion in  $g$ -SiO<sub>2</sub> are the creation, diffusion and annihilation of coordination defects, and can require the collective displacement of hundreds of atoms. The types of defects that dominate the dynamics are dangling bonds, either attached to a Si atom ( $E'$  centers), or to an O atom (non-bridging oxygens); a pair of these defects can easily be created and annealed, with an activation energy that is often similar to what is required for the diffusion of these defects. Moreover, all these mechanisms involve O and Si with almost equal weight, indicating that the two species should diffuse with roughly the same activation barrier. These elementary mechanisms are fundamentally different from those found in amorphous silicon, which underlines the rich diversity in the microscopic dynamics of network glasses.

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